

AIR RESOURCES BOARD

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MEMORANDUM

TO: *John*
John Sanders, Ph.D.
Chief, Environmental Monitoring and Pest Management Branch
Department of Pesticide Regulation

FROM: *Genevieve Shiroma*
Genevieve Shiroma
Chief, Toxic Air Contaminant Identification Branch

DATE: May 25, 1994

SUBJECT: AIR RESOURCES BOARD MONITORING OF CARBOFURAN

In response to a Department of Pesticide Regulation (DPR) request, the Air Resources Board (ARB) staff conducted application site monitoring in Imperial County for carbofuran. The monitoring results and additional background information are included in the enclosures to this memorandum. A chronology of events is Enclosure I. The complete application site monitoring results are included in Enclosure II. We are planning to conduct ambient monitoring of carbofuran in Imperial County early next year.

If you have questions regarding the actual field sampling, please contact Mr. George Lew, Chief, Engineering Evaluation Branch, at (916) 445-0657. For other questions, please contact me at (916) 322-7072.

Enclosures

John Sanders, Ph.D.

May 25, 1994

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Enclosure I

Chronology of Events

Carbofuran Monitoring
Chronology of Major Events

September 1991	DPR transmits to ARB monitoring recommendations for carbofuran.
February 1993	ARB prepares draft work plan for carbofuran sampling and analysis in Imperial County.
February 1993	ARB staff discusses carbofuran use and application sites with representative of Imperial County Agricultural Commissioner's Office.
March 31 - April 2, 1993	Application monitoring conducted in Imperial County.

Enclosure II

Report on Ambient Concentrations near an Application
of Carbofuran in Imperial County

State of California

AIR RESOURCES BOARD

**AMBIENT AIR MONITORING FOR CARBOFURAN IN IMPERIAL COUNTY
DURING SPRING 1993, AFTER AN APPLICATION TO AN ALFALFA FIELD**

Engineering Evaluation Branch
Monitoring and Laboratory Division

Test Report No. C93-013A

Report Date: March 24, 1994

APPROVED:

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This report has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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Ambient Air Monitoring for Carbofuran in Imperial County
during Spring 1993, after an Application to an Alfalfa Field

This report presents the results of ambient air monitoring for carbofuran after a ground application at a selected alfalfa field in Imperial County. Detected concentrations varied from 0.03 to 0.66 ug/m³. The results are based on samples collected by the Air Resources Board Engineering Evaluation Branch staff and analyzed by the Trace Analytical Laboratory, Department of Environmental Toxicology at U.C. Davis. The results have been reviewed by the ARB staff and are believed to be accurate within the limits of the methods.

Acknowledgments

Jack Rogers was the Instrument Technician. Linda Evans of the Imperial County Office of the Agricultural Commissioner assisted in arranging for a suitable field to monitor. Assistance was provided by Lynn Baker and Ruth Tomlin of the ARB's Toxic Air Contaminant Identification Branch. Chemical analyses were performed by the Trace Analytical Laboratory, Department of Environmental Toxicology of the University of California, Davis.

State of California
Air Resources Board

Ambient Air Monitoring for Carbofuran in Imperial County
during Spring 1993, after an Application to an Alfalfa Field

I. INTRODUCTION

At the request of the California Department of Pesticide Regulation (DPR) and the Air Resources Board (ARB) Toxic Air Contaminant Identification Branch, the ARB Engineering Evaluation Branch (EEB) conducted a two-day source impacted ambient monitoring program for carbofuran in Imperial County during the Spring of 1993. As required by AB 1807, this monitoring was conducted to provide DPR with data for the evaluation of the persistence and exposure of airborne pesticides.

The Pesticide Use Report for 1991 indicated the predominant use for carbofuran was alfalfa, followed by grapes, rice and sugarbeets. The peak use for alfalfa was February - March in Imperial County.

II. DESCRIPTION

Carbofuran (molecular weight 221.26 g/mole) is a broad spectrum insecticide used on various crops for a variety of pests. Chemically it is a white, odorless solid with a melting point of 153-154°C. It has a vapor pressure of 3.1×10^{-7} mbar at 20°C. It is nearly insoluble in water and n-hexane, but is soluble in 2-propanol and readily soluble in dichloromethane. The oral LD₅₀ for rats is 11 mg/kg and the dermal LD₅₀ for rabbits is 10,200 mg/kg (1990 Farm Chemicals Handbook). Carbofuran is regulated as a restricted use material under section 6400, Title 3 of the California Code of Regulations, requiring a permit to purchase products containing greater than 10% active ingredient (carbofuran) by weight.

III. SAMPLING LOCATIONS

An alfalfa field of about 70 acres was selected (FIGURE I) by Linda Evans of the Imperial County Office of the Agricultural Commissioner and approved by ARB staff to use for application monitoring. Five samplers were set up: (1) two (collocated) approximately 20 yards north of the field, (2) one approximately 20 yards south of the field (3) one approximately 20 yards east of the field and (4) one approximately 20 yards west of the field. A meteorological station was set up near the southern sampler (FIGURE II). The application occurred on March 31, 1993 and the monitoring continued until the morning of April 2.

The insecticide was applied from west to east using a pickup truck pulling a tank with booms. The application took one hour to complete at the rate of one and one-quarter pints Furadan (containing 44% active

ingredient, carbofuran) per acre. The Notice of Intent is included as APPENDIX I.

IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through XAD-4 resin (see APPENDIX II). The holders were made of Teflon and contained approximately 30 cc of resin. The resin was held in place by installing stainless steel screens on each side of the resin and between the Teflon support rings. Any carbofuran present in the sampled ambient air was captured by the XAD-4 adsorbent. Subsequent to sampling, the resin was transported on dry ice to the Trace Analytical Laboratory (TAL) of the Department of Environmental Toxicology (DET), University of California, Davis for analysis.

Sampling trains designed to operate continuously were set up at the sampling sites identified in FIGURE II. Duplicate samples were obtained from the site designated "N". Resin was changed, as closely as practical, according to the schedule outlined in the QA Plan for Pesticide Monitoring (APPENDIX III).

Each sample train consisted of an XAD-4 resin holder, Teflon fittings and tubing, control valve, train support, and a 12VDC battery-powered vacuum pump. A diagram of the sampling train is shown in FIGURE III. Aluminum foil was wrapped around the holder to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow through the resin holder adjusted with a metering valve to an indicated reading of 12.4 on a flow meter. This was accomplished by attaching a calibrated flow meter to the inlet of the resin holder. A leak check was performed by blocking off the flow meter inlet. Upon completion of a successful leak check, the indicated flow rate was again set at 12.4 and was recorded (if different from the planned lpm) along with date, time and site location. Calibration prior to use in the field indicated that an average flow rate of 16.2 lpm was actually achieved when the flow meter was set to 12.4.

At the end of each sampling period the final indicated flow rate (if different than the set 12.4), the stop date and time were recorded. The XAD-4 resin was then removed from the holder, transferred to a pre-cleaned jar with a Teflon-lined lid and an identification label affixed to each jar. Each jar was then placed in an ice chest containing dry ice until the jars were delivered to the laboratory for analysis.

V. ANALYTICAL METHODOLOGY

The XAD-4 resin recovered from each sampler was analyzed by the TAL staff. The XAD-4 was extracted with 75 ml of ethyl acetate, concentrated, followed by GC separation on a DB-5 megabore column and measurement by a Thermionic Specific (nitrogen/phosphorous) Detector (TSD) (APPENDIX IV). The minimum detection limit was 5 times the baseline noise.

VI. RESULTS

Results for carbofuran are shown in TABLE I and APPENDIX IV. Many of the flow rates decreased from the original set value for the samples in the 5 and 6 series (e.g., 5W, 6N-1, etc.). The reported values (TABLE I) were calculated using the average of the beginning and ending flow rates. The final concentrations were also calculated using the beginning flow rate and the final flow rate separately. This would give minimum and maximum concentrations possible. It was found the resultant concentrations varied from the reported values by no more than plus or minus the least significant digit reported. TABLE II is a summary of the meteorological data collected on site. TABLE III is a pictographic summary of both the meteorological and sampling data. As TABLE I shows, low levels of carbofuran were found. The values were fairly evenly distributed between the lowest and highest measured concentrations, 0.03 to 0.66 $\mu\text{g}/\text{m}^3$.

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the Laboratory Reports for Carbofuran (APPENDIX IV).

All of the procedures outlined in the Pesticide Quality Assurance Plan (APPENDIX III) were followed. The Quality Management and Operations Support Branch (QMOSB) of the ARB conducted a flow audit of the samplers as well as a laboratory audit of the DET at U.C. Davis. This report is included as APPENDIX V. As shown in APPENDIX V, the flow rates were within 2% of the reported rate and the recovery of the spiked samples by DET were from 10% below the spiked level to 5% above the spiked level.

Table I. Carbofuran Monitoring Data

Sample ID	Time (min.)	Volume (m ³)	Amount Detected (ug) [*]	Concentration (ug/m ³)	Collection Time (Approx.)
0W	85	1.37	ND	--	(Background) 3/31/93 0800-0930
0N-1	95	1.53	ND	--	
0N-2	95	1.53	ND	--	
0E	95	1.53	ND	--	
0S	85	1.37	ND	--	
1W	65	1.05	0.3	0.29	(Application) 3/31/93 1000-1100
1N-1	90	1.45	ND	--	
1N-2	90	1.45	ND	--	
1E	85	1.37	0.9	0.66	
1S	90	1.45	ND	--	
2W	165	2.66	1.3	0.49	3/31/93 1100-1400
2N-1	165	2.66	0.9	0.34	
2N-2	165	2.66	0.6	0.23	
2E	170	2.74	0.4	0.15	
2S	165	2.66	ND	--	
2B	BLANK	--	ND	--	
3W	210	3.38	1.8	0.53	3/31/93 1400-1730
3N-1	215	3.46	1.9	0.55	
3N-2	215	3.46	2.3	0.66	
3E	210	3.38	0.9	0.27	
3S	215	3.46	ND	--	
4W	215	3.46	0.9	0.26	3/31/93 1730-2100
4N-1	210	3.38	0.7	0.21	
4N-2	210	3.38	0.7	0.21	
4E	210	3.38	0.5	0.15	
4S	210	3.38	ND	--	
5W	605	9.62	0.3	0.03	3/31-4/1/93 2100-0700
5N-1	605	9.44	0.7	0.07	
5N-2	605	9.44	0.8	0.08	
5E	610	9.70	2.0	0.21	
5S	610	9.70	1.1	0.11	
6W	1410	22.63	0.8	0.04	4/1-2/93 0700-0600
6N-1	1400	20.38	1.3	0.06	
6N-2	1400	22.47	1.3	0.06	
6E	1395	22.18	2.6	0.12	
6S	1380	21.94	1.0	0.05	
6B	BLANK	--	ND	--	

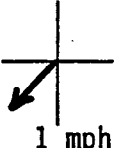

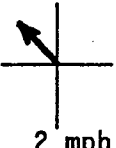

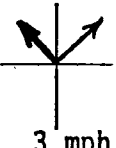
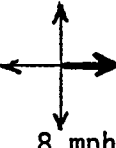
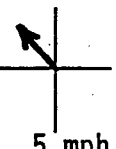
* ND = Not Detected, less than the limit of quantitation, 0.3 ug/sample.

Table II. Carbofuran Meteorological Data

Sampling Period	Date	Time	Wind Speed (mph)	Wind Direction*
0	3/31	0800-0930	1	<u>NE</u>
1	3/31	1000-1100	2	<u>SE</u>
2	3/31	1100-1400	3	<u>SE</u> /SW
3	3/31	1400-1730	5	<u>SE</u>
4	3/31	1730-2100	2	<u>SE</u>
5	3/31-4/1	2100-0700	2	W/NW
6	4/1-4/2	0700-0600	8	W/N/S/E

* indicates direction wind is blowing from. **BOLD** indicates predominant wind direction, if any.

TABLE III. Summary of Carbofuran Application Data ($\mu\text{g}/\text{m}^3$)

<p>(0) [N] <u>ND*</u></p> <p>[W] <u>ND</u>  [E] <u>ND</u></p> <p>[S] <u>ND</u></p>	<p>[N] <u>0.21*</u></p> <p>(4) [W] <u>0.26</u>  [E] <u>0.15</u></p> <p>[S] <u>ND</u></p>
<p>[N] <u>ND*</u></p> <p>(1) [W] <u>0.29</u>  [E] <u>0.66</u></p> <p>[S] <u>ND</u></p>	<p>[N] <u>0.08*</u></p> <p>(5) [W] <u>0.03</u>  [E] <u>0.21</u></p> <p>[S] <u>0.11</u></p>
<p>[N] <u>0.28*</u></p> <p>(2) [W] <u>0.49</u>  [E] <u>0.15</u></p> <p>[S] <u>ND</u></p>	<p>[N] <u>0.06*</u></p> <p>(6) [W] <u>0.04</u>  [E] <u>0.12</u></p> <p>[S] <u>0.05</u></p>
<p>[N] <u>0.60*</u></p> <p>(3) [W] <u>0.53</u>  [E] <u>0.27</u></p> <p>[S] <u>ND</u></p>	

* Average of two collocated samples.

() Indicates sampling period. [] Indicates sampling site represented.

Arrow indicates direction wind is blowing toward. Bold indicates predominant wind direction, if any.

ND = not detected, less than the limit of quantitation, $0.3 \mu\text{g}/\text{sample}$.

Figure I. Carbofuran Monitoring Area

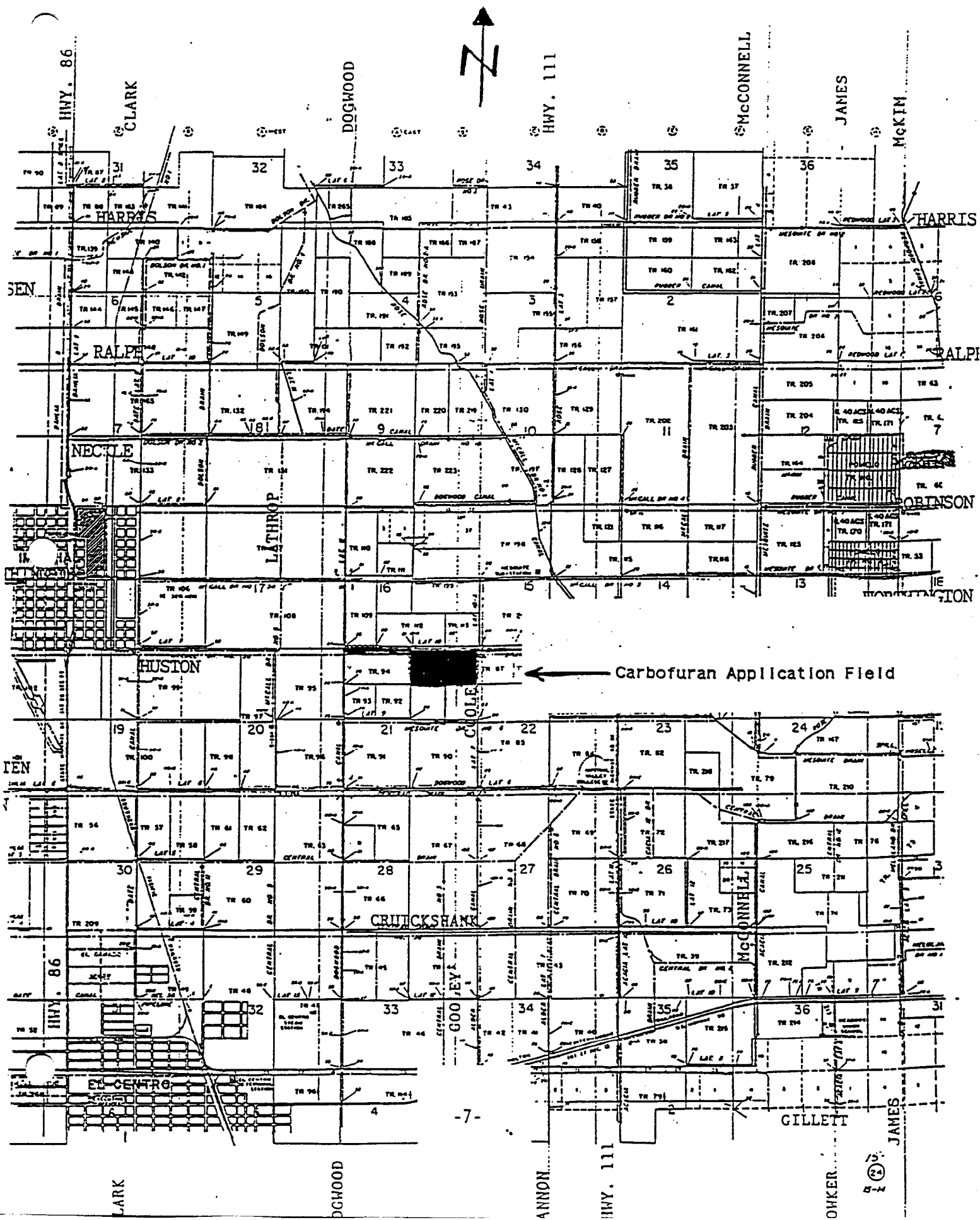
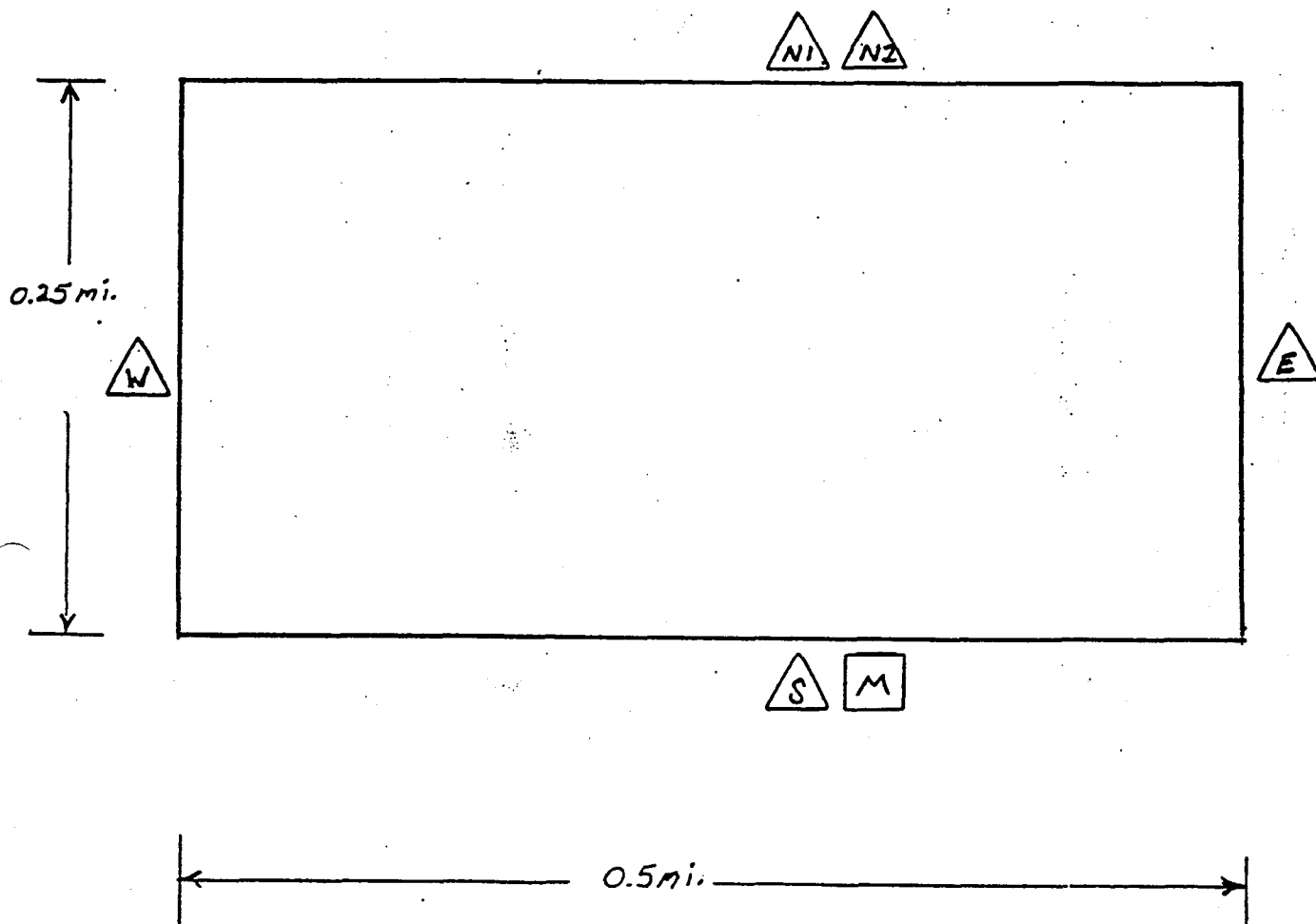


Figure II. Carbofuran Monitoring Sites





Legend	
	Sampling station
	Met. station
distances approximate	

Figure III. Carbofuran Monitoring Apparatus

